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STUDIES ON THE ELECTROCHEMICAL PROPERTIES OF COPOLYMERS OF MALEIC ACID, VI

Conductometric Behaviors

BY KAZUO MONOBE

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Conductometric behaviors of the copolymers of maleic acid with either vinyl acetate or styrene were studied. The polydibasic characteristic of the titration curves were discussed with the analytical aspects. On the other hand, the equivalent conductance of the polyanions were approximately evaluated from the titration results at low values of α and from the conductance-concentration curves at $\alpha=1$.

Introduction

In the previous papers[1], the polydibasic properties of maleic acid copolymers were studied by means of the potentiometric titration. In the preceding paper[2], we studied the copolymers as polyelectrolytes whose viscosities were modified by the presence of charges. We now turn to the study of electrical properties: conductometric behaviors. We may obtain some useful knowledge[3] from the study on conductance behavior over that from the study on equilibrium process such as potentiometric behavior. However, attention is mainly arrested here on the polydibasic characteristics for the two copolymers of maleic acid given by the conductometric titration, while the conductance as a function of concentration is also studied briefly.

Experimentals

The copolymers used here were the fractionated samples, MA–VAc–F_3 (maleic acid–vinyl acetate copolymer) and MA–S–F_7, (maleic acid–styrene copolymer) described in the previous paper[4].

The conductance measurements were carried out with a Yanagimoto conductometer of photo cell type (1000 cycles) at 25.0±0.05°C and in nitrogen atmosphere. The two electrolytic cells were used,——the one for titration was a terex glass vessel enclosing the platinized electrodes and the other for the diluted solution was a terex glass vessel enclosing the unplatinized electrodes. The cell constants were 0.458 and 0.348 at 25°C, respectively. These cell constants were deter-

1) K. Monobe, *This Journal*, **30**, 138, 145 (1960)
2) K. Monobe, *ibid.*, **31**, 50 (1961)
3) Parameters such as shapes and sizes of molecule, which are intrinsically inaccessible to thermodynamic investigation, are essential in a consideration of conductance.
4) K. Monobe, *This Journal*, **30**, 156 (1960)

mined by the conductance measurements on KCl aqueous solutions whose equivalent conductances were calculated by the equation of Shedlovsky[5],

$$\frac{\Lambda+59.79C^{\frac{1}{2}}}{1-0.2274C^{\frac{1}{2}}}=149.86+141.9C+29.24C\ \log C-180.6C^{2}.$$

The specific conductance κ of the water used was $0.8\times10^{-6}\mathrm{ohm}^{-1}\mathrm{cm}^{-1}$.

Results and Discussion

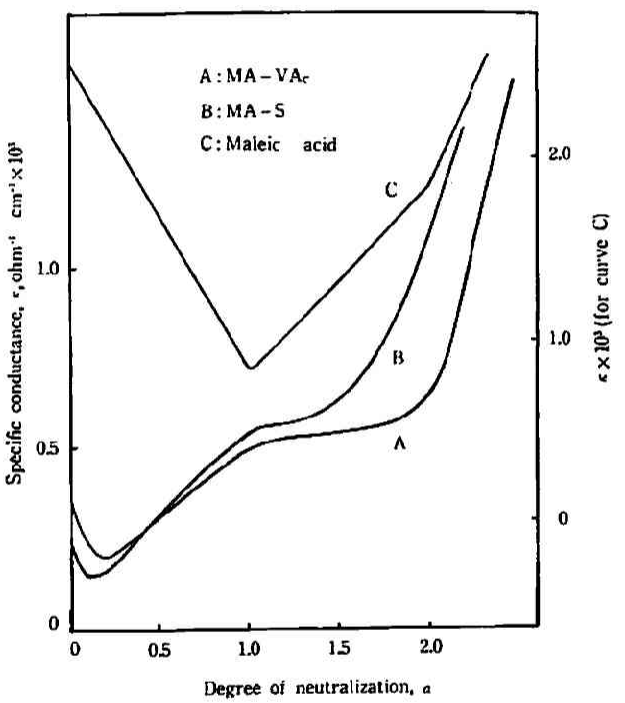

Fig. 1 Conductometric titration curves at 25°C

curve A: MA-VAc $0.981\times10^{-2}M$
curve B: MA-S $0.983\times10^{-2}M$
curve C: Maleic acid $1.00\times10^{-2}M$

1 Conductometric titration Fig. 1 shows the results of conductometric titration for the two copolymers, MA-VAc and MA-S, together with that for the maleic acid at the concentration of $0.01M$. As shown in Fig. 1, the titration curves of the copolymers (curves A and B) are both W-shape, while that of the maleic acid (curve C) is V-shape. In these titration curves, the range of neutralization from $\alpha=0$ to $\alpha=1$ shows the neutralization processes of the primary carboxyl groups and the range from $\alpha=1$ to $\alpha=2$ shows that of the secondary carboxyl groups. Appearance of minimum on the titration curves for the copolymers at low values of $\alpha(\alpha\simeq0.2)$ is based on the even balance between decreasing hydrogen ions due to the selfionization of the polyacids and increasing sodium ions in the couse of the neutralization. This behavior is seen also in the polyacrylic acid[6] and is generally seen in the weak monomeric acids such as acetic

5) T. Shedlovsky, A. S. Brown and D. A. MacInnes, *Trans. Electrochem. Soc.*, 66, 165 (1934)
6) H. P. Gregor and M. Fredrick, *J. Polymer Sci.*, 23, 451 (1957)

acid. After this minimum point, the specific conductance κ increases with α ($0.2<\alpha<1.0$). However, the two curves for copolymers cross with each other; at nearly the same concentration of 0.01 M, the specific conductance of MA–S copolymer aqueous solution (curve B) is lower than that of MA–VAc copolymer aqueous solution (curve A) in the range of $0.4>\alpha$, but this relation is reversed in the range of $0.4<\alpha$. In this range of neutralization, the counter-ion binding within a polyion increases gradually with α, since the increased net charges on a polymer chain produce the stronger electrostatic potential as α increases. Therefore, we may apparently attribute the difference of the increasing rate of κ between MA–S and MA–VAc copolymers to that of the counter-ion binding, assuming that the conductances of polymers are nearly the same between the two copolymers.

These counter-ion binding behaviors for the copolymers become so marked in the next step of titration curves that κ remains nearly constant in spite of the increase of α for MA–VAc copolymer. In this range of neutralization, $1<\alpha<2$, there occurs the counter-ion binding due to the strong nearest neighboring electrostatic interactions in addition to the electrostatic forces due to the increased potential which comes from the whole charged groups on a polymer molecule. In MA–S copolymer, it depends on the increased conductance of the hydroxyl and sodium ions which come from the hydrolysis of the polysalt that κ increases sharply with α before the neutralization point, $\alpha=2$. The strong hydrolysis tendency of MA–S copolymer has been also observed in the previous paper on potentiometric titration[1]. On the other hand, the association of sodium ion due to the neighboring charge in the monomeric disodium maleate is not so large compared with the binding in the copolymers.

The observed specific conductances of the copolymer solutions, κ, are the sum of the contributions of counter-ions, κ_c, and polyanions, κ_p;

$$\kappa=\kappa_p+\kappa_c. \tag{1}$$

One may calculate the equivalent conductances for the copolymers by the equation,

$$\Lambda_p=\frac{1000\kappa_p}{C}, \tag{2}$$

where Λ_p and C are the equivalent conductance and the equivalent concentration on the basis of α values, respectively. κ_p is the specific conductance of the polyanion. We shall assume here the complete dissociation of the polysalts and independent migration at low values of α. Thus, we calculated the approximate values of Λ_p according to Equations (2) and (1), where the limiting equivalent conductance, $\Lambda^\circ_{Na^+}=50.1$ and $\Lambda^\circ_{H^+}=350$ at 25°C, were used in the calculation of κ_c. At this time, the hydrogen ion concentrations were calculated from the potentiometric titration curves measured simultaneously. The values obtained for the copolymers of maleic acid are $\Lambda_p=36.2\,\mathrm{ohm^{-1}cm^{-1}equiv^{-1}}$ for MA–VAc at $\alpha=0.26$ and $\Lambda_p=30.2$[7] $\mathrm{ohm^{-1}cm^{-1}equiv^{-1}}$ for

7) Assuming that the Λ_p value obtained for MA-S at $\alpha=0.21$ is constant for all other values of α, we calculated the fraction of bound counter-ions according to the Equation[6], $\beta=1-\frac{\kappa}{\kappa_p^\circ+\kappa_c}$. The result gave somewhat lower value than that obtained by Wall[8].

8) F. T. Wall and R. H. Doremus, *J. Am. Chem. Soc.*, **76**, 1557 (1954)

MA-S at $\alpha=0.21$. These values nearly accord with the results expected from the conductance —concentration curves in the next paragraph and also are lower than the corresponding value of polyacrylic acid[6] ($\Lambda_p=40$).

2 Equivalent conductance as a function of concentration We measured the specific conductance as a function of concentration at a given degree of neutralization. We shall show here the conductance curves for the two copolymers at $\alpha=1.0$ in order to know approximately the limiting conductances Λ°_p. Fig. 2 shows the plots of the equivalent conductance Λ against $\sqrt{C}$ for the two copolymers. Λ was calculated by the equation,

$$\Lambda=\frac{1000\kappa}{C},$$

where C was represented by the equivalent counter-ion concentration at $\alpha=1$. As shown in Fig. 2, the two curves are concave up with dilution and the extrapolations to $C=0$ come down

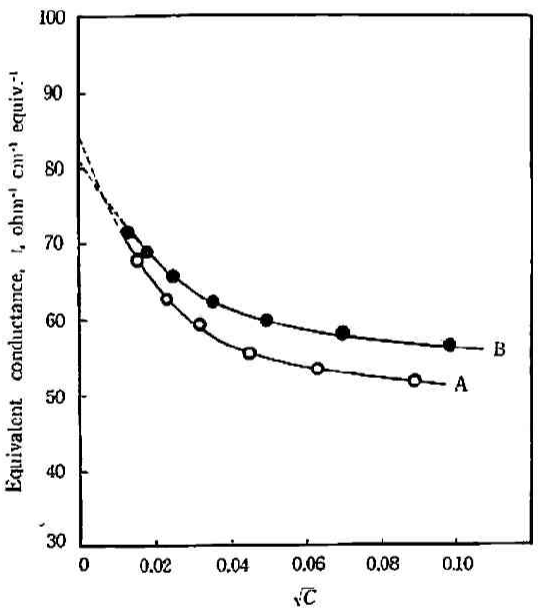

Fig. 2 Equivalent conductance as a function of concentration at 25°C

curve A: MA-VAc copolymer at $\alpha=1.0$
curve B: MA-S copolymer at $\alpha=1.0$

in the neighborhood of $\Lambda=80$. Thus, we obtain approximately $\Lambda^\circ_p=30\sim35$ for the two copolymers by the additivity of limiting equivalent conductance, $\Lambda^\circ=\Lambda^\circ_p+\Lambda^\circ_c$, where Λ°_c is the limiting equivalent conductance of the counter-ion; $\Lambda^\circ_{Na^+}=50.1$ at 25°C.

3 Analytical aspects of the copolymers The conductometric titration curve for MA-VAc copolymer in Fig. 1 shows the sharp break at the points corresponding to $\alpha=1$ and $\alpha=2$. Thus, we can readily obtain the half neutralization point and the neutralization point by the intersections of the proper two straight lines in the titration curve, respectively. And also we can ascertain that the one point corresponding to $\alpha=2$ is exactly twice the other point corresponding to $\alpha=1$. This is no longer expected when the saponification of the acetyl group in the copolymer and the successive intramolecular lactonization occur. As for these reactions

which would occur at high temperature, the analytical results of conductometric titrations will be shown in the succeeding paper.

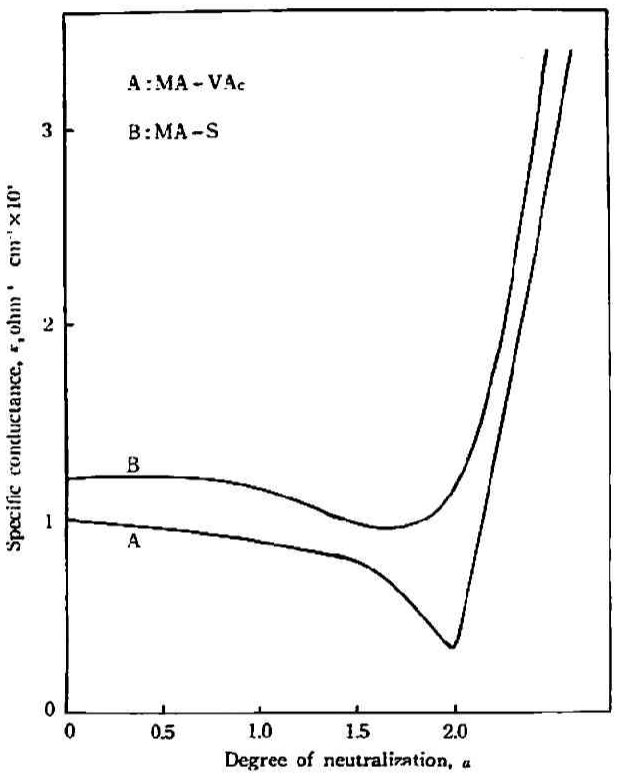

Fig. 3 Conductometric titration curves in pyridine-aqueous (1:1) solution at 25°C

curve A: MA-VAc
curve B: MA-S

On the other hand, in MA-S copolymer, it is very difficult to determine the neutralization point as shown in Fig. 1. We can obtain the neutralization point by doubling the half neutralization point determined, which coincides[1] also with the end point by phenolred in 0.01 *M* aqueous solution.

We have known the other method[1] to determine the neutralization point for MA-VAc copolymer; phenolphthalein indicator method in pyridine aqueous solution (1:1). We carried out the conductometric titration for the two copolymers in the pyridine aqueous solution (1:1). The results obtained are shown in Fig. 3. A monobasic characteristic of the titration curves which show no distinct inflection at $\alpha=1$ may be based on the presence of pyridine as a weak base. However, the sharp break at the point corresponds to $\alpha=2$ for MA-VAc copolymer, suggests analytical usefulness.

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